Electronic Supplementary Information for

Facile synthesis of a mesoporous Co$_3$O$_4$ network for Li-storage via thermal decomposition of an amorphous metal-complex

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Experimental section

Synthesis

Porous ZnCo$_2$O$_4$: 0.833 g Co(NO$_3$)$_2$·6H$_2$O, 0.426 g Zn(NO$_3$)$_2$·6H$_2$O and 1.750 g glycine (C$_2$H$_5$NO$_2$) were dissolved in 10 mL deionized water in a crucible to form a solution, which was then transferred to a preheated furnace maintained at 400 ºC for ca. 16 min to finish the decomposition reaction, which resulted in a black foam. The as-combusted sample was then heated at 480 ºC for 2 h in air at a heating rate of 5 ºC min$^{-1}$ to achieve finally the porous ZnCo$_2$O$_4$.

Porous NiO: 1.250 Ni(NO$_3$)$_2$·6H$_2$O and 1.750 g glycine (C$_2$H$_5$NO$_2$) were dissolved in 10 mL deionized water in a crucible to form a solution, which was then transferred to a preheated furnace maintained at 400 ºC for ca. 16 min to finish the decomposition reaction, leading to a black foam. The as-combusted sample was then heated at 550 ºC for 1 h in air at a heating rate of 5 ºC min$^{-1}$ to achieve finally the porous NiO.

Characterization

X-ray diffraction (XRD) measurements were conducted on a XRD-6000 diffractometer (SHIMADZU) with Cu Kα radiation, operated at 40 kV, 40 mA ($\lambda=$0.15406 nm). The powder morphology was observed using a field emission scanning electron microscopy (FE-SEM, with EDS capabilities, Hitachi S-4800, Tokyo, Japan) and a FEI-F20 transmission electron microscopy (TEM, FEI, USA) working at 200 kV. A STA-449F3 instrument (NETZSCH-Gerätebau GmbH, Germany) was used to carry out the thermogravimetric (TG) analysis of the as-combusted samples in air atmosphere at a heating rate of 5 ºC min$^{-1}$ from room temperature to 800
ºC. The Brunauer-Emmett-Teller (BET) approach using adsorption data was utilized to determine the specific surface area. The sample was degassed at 150 ºC for 14 h to remove physisorbed gases prior to the measurement.

**Lithium storage test**

The working electrodes were prepared by a slurry coating procedure. The slurry consisted of 80 wt. % Co₃O₄ powders, 10 wt. % acetylene black, and 10 wt. % polyvinylidene fluoride (PVDF) dispersed in N-methyl pyrrolidone (NMP), and was coated on a copper foil, which acted as a current collector. The active material (Co₃O₄) was 0.4–0.6 mg/cm² on each electrode and the coating thickness was ca. 3.5 µm. Electrodes with a much higher mass loading of 1.5–2.5 mg/cm² were also characterized. The film was dried at 120 ºC for 12 h in vacuum. The cells were assembled in an argon-filled glove box using Li foil as a counter electrode and polypropylene (PP) film (Celgard 2300) as a separator. The electrolyte was 1 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The charge–discharge tests were conducted on a LAND 2001A system at a current density of 100 mA g⁻¹ and 1000 mA g⁻¹ between 0.005 V and 3.0 V. The cyclic voltammetry was performed on a CHI660D electrochemical workstation.

![Fig. S1](image-url) The decomposition process of the precursor solution: (a) boiling of the pink solution (0 min), (b) changing to blue and bubbling (6.0 min), (c) bubbling, decomposition and release of gases (7.0 min), and (d) the formation of the black product (13.5 min).
**Fig. S2** EDS spectrum of the as-synthesized cobalt-based complex. The Al element in EDS spectrum is from the SEM holder.

![Co 2p spectrum](image1)

![O 1s spectrum](image2)

![C 1s spectrum](image3)

![N 1s spectrum](image4)

**Fig. S3** High-resolution XPS spectra of as-synthesized cobalt-based complex: (a) Co 2p, (b) O 1s, (c) C 1s, and (d) N 1s.
**Fig. S4** The as-synthesized cobalt-based complex and the corresponding elemental mappings of Co, O, C, and N.
**Fig. S5** N 1s high-resolution XPS spectrum of the porous Co$_3$O$_4$.

**Fig. S6** XRD patterns of the as-synthesized cobalt-based complex after calcination at different temperatures for 1 h: (a) 450 °C and (b) 550 °C.

**Fig. S7** SEM images of the as-synthesized cobalt-based complex after calcination at different temperatures for 1 h: (a) 450 °C and (b) 550 °C.
Fig. S8 The cyclic voltammetry (CV) curves of the porous Co$_3$O$_4$ scanned at a rate of 0.1 mV s$^{-1}$. 

Fig. S9 Cycling performance of commercial Co$_3$O$_4$ nanoparticles (30 nm in size, Aladdin Reagent Co. Ltd., China) at a current density of 100 mA g$^{-1}$. The mass loading of the active material (Co$_3$O$_4$) was ca. 0.5 mg cm$^{-2}$. 

Fig. S10 The discharge–charge profiles of the porous Co$_3$O$_4$ at different current density. The rate performance is measured after the cycling test at 1000 mA g$^{-1}$ for 390 cycles to stabilize the capacity because discharge capacity of the present porous Co$_3$O$_4$ firstly decreases and then gradually increases during the cycling (Fig. 6b and 6c).
**Fig. S11** (a) The discharge–charge profiles of the porous Co$_3$O$_4$ at different current density. (b) Cycling performance of the porous Co$_3$O$_4$ network at a current density of 1000 mA g$^{-1}$. (c) Cross sectional SEM image of an electrode, showing the thickness of the coating is ca. 13 μm. The active material (porous Co$_3$O$_4$) was 1.5–2.5 mg cm$^{-2}$ on each electrode.

**Fig. S12** SEM images of porous ZnCo$_2$O$_4$ (a) and porous NiO (b).
Fig. S13 XRD patterns of porous ZnCo$_2$O$_4$ and porous NiO.